

Measurement of Fallout ^{239}Pu Levels in Urine Samples by Fission Track Analysis*

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ABSTRACT

A Fission Track Analysis (FTA) method for assessing ^{239}Pu in urine samples was first developed at Brookhaven National Laboratory (BNL) in 1988; it then had a detection limit of 100 aCi (3.7 μBq). Since that time, several steps were introduced that increased chemical recovery and lowered the detection limit to less than 10 aCi per sample. These improvements include a process of micro-column separation of plutonium in the final stages (patent applied for). The improved FTA method was applied to 22 urine samples from male staff at BNL. The results showed that ^{239}Pu from fallout excreted in urine was 33 ± 11 aCi (1.2 μBq) per day.

Introduction:

In 1988, Moorthy published details of the Fission Track Analysis (FTA) method for determining ^{239}Pu in urine samples [1]; a detection limit of 100 aCi (3.7 μBq) was attained. Since then, several automated steps were introduced to increase chemical recovery, to reduce false positive results, and to lower the detection limit.

The Nuclear Test Personnel Review Program (Defense Nuclear Agency) is concerned with the internal dose in U.S. veterans who were exposed to ^{239}Pu during atmospheric nuclear tests, and during the occupation of Hiroshima and Nagasaki, Japan. Direct measurements of intake through air sampling, or excretion through urine bioassay, were rarely made during the weapons-testing era. Other techniques, including inductively coupled plasma mass spectrometry (ICP/MS), do not yet have the sensitivity to measure background or fallout levels of plutonium in

* This work was performed under the auspices of the U.S. Department of Energy under Contract DEAC0276CH00016

urine samples unless very large volumes are analyzed.

Before assessing the dose in veterans and also establishing the background levels of ^{239}Pu in a representative population, we analyzed urine samples from male employees at BNL using the newly improved FTA method. Some of these persons had prior exposures to plutonium, though, at the time of analyses, this was not known to us.

Method:

Experience with analyzing thousands of urine samples for the past eight years using the FTA method enabled us to introduce several steps to improve it. Except for some automated procedures, the overall protocol is the same as detailed in the original publication (1). The three areas where automation was introduced are 1) fire-polishing of Suprasil-fused silica slides, 2) preparing "uranium-free" 8N HNO_3 and 6N HCl , and 3) using a 10 μl column in the second stage. Final separation of "residue-free" plutonium is carried out with a 10 μl Teflon- or a 12 to 15 μl quartz-column.

The FTA method entails the co-precipitation with rhodizonic acid of Pu from a liter of urine. The precipitate is dried at low heat to drive out the alcohol, dissolved in 8N HNO_3 , and evaporated to dryness with additions of more acid and H_2O_2 to decompose any organics. The clear solution in 8N HNO_3 , with Pu converted to a fourth valency state, is passed through 6 ml of an anion exchange column and washed with sub-boiled-distilled (SBD) 8N HNO_3 and SBD 6N HCl acids, and the Pu is eluted with 6N HCl -0.1N HI . The solution is evaporated to dryness and dissolved in 300 μl of SBD 8N HNO_3 . All subsequent operations are performed inside a Class 100 hood. After adding about 50 μl of SBD 8N HNO_3 containing nitrous acid, the sample is introduced by a syringe pump into a closed loop, consisting of Teflon tubing, valves, and a 10 μl micro-column. A patent has been applied for this micro-column procedure (2). The sample is infused against gravity through the micro-column that contains specially sieved anion exchange resin, at a pressure of about 80 psi. The column is cleaned with several column volumes of

uranium- and residue-free SBD 8N HNO₃, followed by residue- and uranium-free SDB 6N HCl. The Pu is eluted with 4N HCl-0.008N HF in 3 drops of 15 µl each, on an area of 1 cm² of a cleaned, fire-polished silica or Suprasil surface. The samples are evaporated, vacuum-sealed, and irradiated at a thermal neutron fluence of 9E16 n/cm² in one of the reactors at BNL. After irradiation, the slides are cleaned and etched in HF to enlarge the tracks which then are counted in a semi-automated counting system. Synthetic urine blanks and spikes, ranging from 25 to 200 aCi, are analyzed similarly to obtain a calibration curve. From the calibration curve, the background tracks and the conversion factor of tracks per aCi are derived and used to obtain aCi levels in urine samples.

Results:

The change from manual to auto-firepolishing of the silica surface of the slide did not change the background appreciably. The slide's background is 1.9 ± 2 tracks per cm² (n = 74) and can be favorably compared to the background found using Lexan (3) with a track background of 12 ± 5 tracks per cm² (n = 32).

Table 1 lists the uranium concentrations of different acids prepared by various methods. Teflon-column-produced 8N HNO₃ and 6N HCl were used in this work; the latter also had less than 10 ppq of uranium.

Based on 8 synthetic urine blanks and 12 spikes, the average synthetic urine background is 16.9 ± 3.8 tracks with a slope of 1.28 tracks/aCi. The MDL (3σ) is about 9 aCi per sample. Table 2 shows the results from the baseline urine samples that were collected from staff members.

Four of the 22 samples had more than 100 aCi per day's urine. Afterwards, we learned that the volunteers providing these samples had reported prior occupational exposure to plutonium, though at the time of analysis, it was not known to us. From the remaining 18 samples, it was concluded that the fallout ²³⁹Pu excretion is 1.2 µBq (33 aCi) per day. This level

compares well with that of researchers elsewhere (3) who measured 4 liters of urine and reported a value of 0.6 $\mu\text{Bq/liter}$.

Table 1 U Concentration (in ppq) in Various 8N HNO₃ Acids

Commercially Distilled	Sub-boiled Distilled	(Column-cleaned Nitric acid)	
		Manually prepared (60 ml Suprasil)	Automated (350 ml Teflon)
11,500 ppq	600 ppq	30 ppq	<10 ppq

Table 2 Results of 22 BNL Baseline Samples

Number of Samples	²³⁹Pu Excreted ($\mu\text{Ci/day}$)
8	<MDL
10	33 ± 11
4	>100

References:

- (1) A. R. Moorthy, C. J. Schopfer and S. Banerjee, Analytical Chemistry, 1988, 60, 857A.
- (2) A. R. Moorthy and R. M. Doty, Patent applied, 1996.
- 3) M. E. Wren, N. P. Singh and Y. H. Xue, Radiation Protection Dosimetry, 53, p. 81.